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Literature Review on Occurrence and Methodology for Determination of Nickel, Chromium, Manganese, and Arsenic Species in Air

Battelle Columbus Labs., OH

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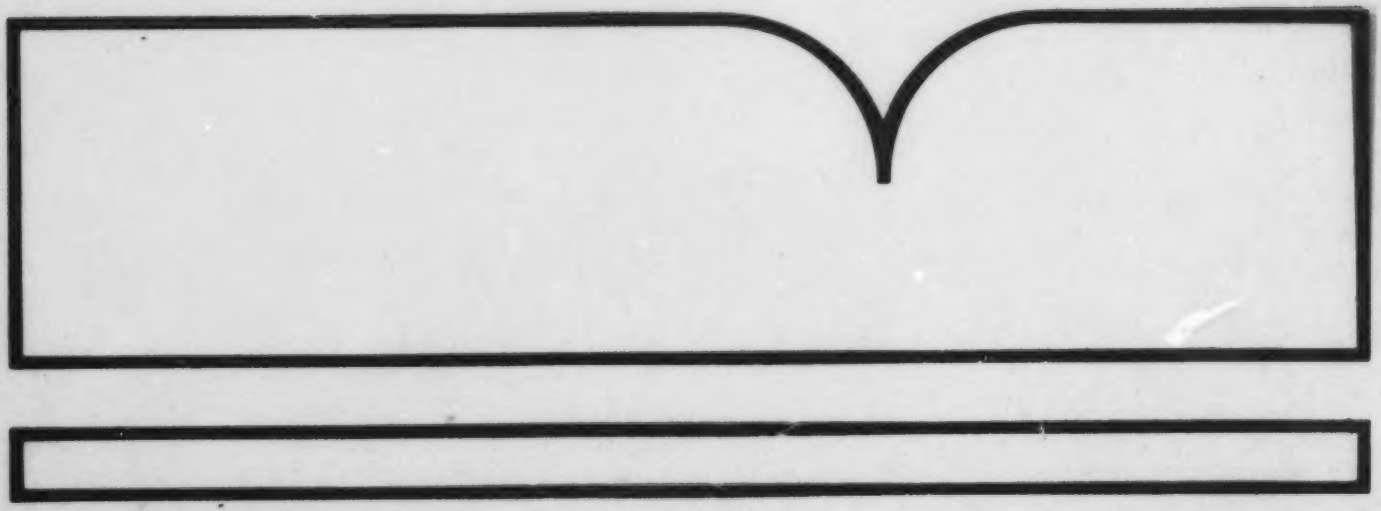

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A LITERATURE REVIEW ON OCCURRENCE AND METHODOLOGY FOR DETERMINATION OF NICKEL, CHROMIUM, MANGANESE, AND ARSENIC SPECIES IN AIR

by

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16. ABSTRACT

A critical literature review of the state of the art for speciation of arsenic, chromium, manganese, and nickel in atmospheric samples was performed. Techniques for distinguishing the compound forms and valence states of these metals were critically assessed. Advantages and limitations of the various speciation approaches were addressed. Three basic types of speciation procedures were identified: a) direct analysis of particulate matter, b) speciation of inorganic compounds after dissolution, and c) sequential or selective extraction. Direct analysis techniques offer the possibility of determining specific compounds but are limited in sensitivity. The latter two techniques cannot determine specific inorganic compounds because of the inclusion of a dissolution step. However, such techniques may give useful information and are more generally applicable than direct analysis techniques. In a few cases (e.g., arsine), compounds may exist in the gas phase and can therefore be readily distinguished from other compound forms of the element.

The literature review included manual searches of Chemical Abstracts, Citations Index, Analytical Abstracts, Air Pollution Abstracts, and selected environmental journals for the period 1968 to 1983.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Inorganic compounds contaminating the atmosphere are usually present in particulate matter and to a lesser extent as vapors and gases. Their capture and subsequent analysis by current monitoring methods usually identifies the elements present, but it is rarely possible to identify the compound(s) in which the element exists or the oxidation state of the element in the compound. This study was undertaken to assess the methods presently employed and to make recommendations as to which methods could be refined for determination of selected inorganic compounds.

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ABSTRACT

A critical literature review of the state of the art for speciation of four metals in atmospheric samples was performed. The four metals of concern were arsenic, chromium, manganese, and nickel. Instrumental and wet chemical techniques for distinguishing the compound forms and valence states of these metals were critically assessed. Advantages and limitations of the various speciation approaches were addressed and recommendations are provided for future research to develop speciation procedures.

Three basic types of speciation procedures identified were: a) direct analysis of particulate matter, b) speciation of inorganic compounds after dissolution, and c) sequential or selective extraction. Direct analysis techniques offer the possibility of determining specific compounds. However, such techniques are often limited in terms of sensitivity and frequently only surface concentrations can be determined. The latter two techniques cannot determine specific inorganic compounds because of the inclusion of a dissolution step. However, such techniques may give useful information and are more generally applicable than direct analysis techniques. In a few cases, e.g., arsine; compounds may exist in the gas phase and can because of differences in physical state be readily distinguished from other compound forms of an element.

The literature review included manual searches of Chemical Abstracts, Citations Index, Analytical Abstracts, Air Pollution Abstracts, and selected environmental journals. Literature from the period 1968-1983 was included in the survey.

This report was submitted in fulfillment of Contract No. 68-02-3745 by Battelle Columbus Laboratories under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from March 1, 1983 to September 1, 1983, and work was completed as of September 1, 1983.

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SECTION 1

INTRODUCTION

There is an increasing awareness by environmental scientists of the importance of analytical methodologies which differentiate and determine the chemical forms of metal pollutants in the ambient atmosphere and near point emission sources. This is due to the great differences in health effects of different forms of the same element, e.g., As(III) and As(V). Potentially the trace metals of interest can be present in compound forms in the gaseous phase and in both compound and nonstoichiometric solid phases. The latter are much more common for the elements of concern in this study, i.e., As, Cr, Mn, and Ni. However, nickel carbonyl, arsine (AsH_3), and cyclopentadienyl manganese tricarbonyl might be found in the gas phase near some specific sources.

Speciation of environmental samples is a very difficult inorganic analytical problem for several reasons. The chemical compositions of atmospheric pollutant samples are very complex, containing some 70 to 80 detectable elements[1-3] which may combine to form hundreds of chemical compounds and thousands of mixtures. The concentrations of the trace elements in the atmosphere are low, e.g., at µg/g levels in particulate matter, thus frequently taxing sampling and analytical capabilities to provide reliable determinations on even the total elemental content. The commonly used analytical methods are designed to provide elemental analyses, not information on compound type or valence states. Other techniques yield information on types of ions present. However, both ionic and elemental techniques commonly break down the inorganic forms into their ionic or atomic states by procedures that change the chemical forms of the sample to facilitate the determination of the total concentration of the element. Until recently there has been little substantive interest in funding the development of analytical efforts necessary to differentiate between trace metal compound species in any media, particularly in air samples. Finally, atmospheric samples often contain components that can interact rapidly with each other necessitating use of sampling methodologies that would minimize such interaction and preserve the integrity of the components as they exist in the ambient air or source emissions. In general, covalent inorganic species exist as discrete compounds, are frequently volatile at ambient temperature, and may be determined by techniques used in organic analysis. These species will be found predominantly in the gas phase or perhaps adsorbed on particulate matter. However, the majority of the metal species of interest will be found in ionic compounds or nonstoichiometric mixtures in the particulate matter. Some of these ionic compounds and mixtures are not soluble in mild solvents and very strong reagents are required to dissolve them.

Despite the difficulties cited above, some efforts have been made to develop and apply methodologies for the determination of metal species in atmospheric samples. It was the objective of this program to conduct a comprehensive and critical review of the relevant information in the published literature on the subject of certain metal species occurring in the air and methods for determining these species. The metals of interest are As, Cr, Ni and Mn. Some specific compounds, deemed of particular interest by the U.S. EPA Project Officer, are listed in later sections. Determinations of both the valence states (oxidation states) of these metals and the type of metallic compounds are of interest.

This review is presented in five major sections, including the Introductory section (Section 1), Conclusions (Section 2), and Recommendation sections (Section 3). The fourth section presents an overview of methods suited to, or used for, speciation of metals in atmospheric samples. The fifth section lists the chemical and physical properties of the four trace metals, valence states, oxidation states, and compounds deemed of interest by the U.S. EPA Project Officer. Whenever possible the occurrences of the species in the atmosphere, possible sources and logical reactivities and transformations that might occur in the atmosphere are addressed.

The state-of-art and research and development needs are summarized in the Conclusions and Recommendation Sections.

SECTION 2

CONCLUSIONS

The most significant conclusion of this study is that very few analytical techniques show promise for the determination of specific inorganic compounds in ambient air. Indeed, the most reliable compound methods would apply only to volatile species, e.g., gas chromatography. Instead, one must rely on less specific methods which provide information concerning valence state, e.g. solubility in various extractive media to infer the inorganic compound originally present. In virtually all cases cation and anion analysis data, e.g., by atomic absorption spectroscopy, ion chromatography, must be gathered to aid in the interpretation of data from speciation techniques.

The speciation methods described in the literature can be roughly classified into three groups as shown in Figure 1 and summarized below:

(a) Direct analysis of the particulate material
(b) Speciation of inorganic components after dissolution
(c) Sequential or selective extraction and analysis.

Direct analysis techniques include X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), etc. The direct analysis techniques offer the possibility of determining specific inorganic compounds whereas the other two approaches cannot due to the dissolution process. However, most of the direct analysis techniques suffer from one or more of the following limitations: (a) detection of only surface compounds, (b) poor sensitivity, (c) detection of only crystalline materials, and (d) poor discrimination between similar inorganic compounds. Some direct analysis applications have been reported for Cr, Mn, and Ni compounds. However, much more research must be conducted to establish whether or not such approaches could be applied to ambient air analysis.

Speciation procedures for dissolved inorganics, particularly in water samples, have been widely reported for arsenic; and these methods appear to warrant further study. The particular extraction process preceding the application of these techniques must be validated using authentic compounds with known valence states to ensure preservation of the original form, e.g., valence state, of the element of interest.

Selective and/or sequential extraction procedures have been widely applied to solid samples but have not been validated. These schemes appear to be promising due to their simplicity and relevance to health effects but

require extensive validation as described for the speciation techniques in the previous paragraph.

SECTION 3

RECOMMENDATIONS

On the basis of the findings presented in the subsequent sections, the areas which appear most promising for speciation of the elements of interest are:

As - Solution phase procedures such as electrochemistry and chromatography have considerable promise for arsenic speciation. Further studies need to be conducted to develop and evaluate extraction procedures which can dissolve the arsenic compounds completely without altering their form, e.g., valence state.

Cr - X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) shows some promise for Cr speciation but is limited in that only surface analysis data are obtained. Solution phase techniques suffer from the difficulty encountered in attaining quantitative dissolution of Cr in the sample. Various colorimetric and electrochemical procedures are suitable for distinguishing Cr(III) and Cr(VI), if suitable dissolution procedures can be identified. Further research should be conducted to compare the performance of several of these methods for ambient air analysis. The extraction approach employed would also require validation using authentic compounds of interest.

Mn - Very few promising approaches are available for Mn speciation. Negative ion secondary ion mass spectroscopy (SIMS) may warrant further evaluation. Electron spin resonance (ESR) and nuclear magnetic resonance (NMR) are also worthy of at least cursory evaluation. Solution phase speciation methods do not appear promising. Consequently, sequential and/or selective extraction is probably the most useful area for further research. Several such schemes have been reported and should be further evaluated and/or refined using authentic Mn compounds of interest.

Ni - Selective and/or sequential extraction appears to be the most promising area for further research. A few direct analysis, e.g., X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and solution phase speciation procedures, e.g., high performance liquid chromotography (HPLC) after complexation may also warrant further study.

In view of the lack of routine, validated methods for the inorganic compounds of interest, any further work in this area should apply several alternate approaches to determine the validity of the data. In addition, elemental and anion data must be collected to aid in the interpretation of data from speciation procedures.

There are more effective techniques available for speciation of volatile inorganic compounds than for the nonvolatile species. Volatile metal carbonyls can be separated from particle bound metal compounds during the sampling process. Instrumental methods such as chemiluminescence, mass spectrometry, and gas chromatography with element specific detection appear to offer good sensitivity for these volatile species. These methods warrant further evaluation and refinement, e.g., preparing quantifiable volatile derivatives.

SECTION 4

OVERVIEW OF INORGANIC SPECIATION

Inorganic speciation, in the ideal case, refers to the determination of the identities and concentrations of specific compound forms of a particular element of interest. Unfortunately, state-of-the-art technology does not directly provide such detailed information except in a very few selected cases, mainly for volatile compounds. Consequently researchers in this field have been forced to conduct speciation efforts indirectly with a considerable amount of judgment, extrapolation, and inference being required.

Within this document only the analytical process will be addressed in detail. Generally conventional sampling techniques, i.e., filtration/impaction, are assumed for particulate matter. Sampling for the few volatile compound forms, e.g., metal carbonyls, will be discussed at appropriate points in the document. A diagram of the analysis approaches generally employed for inorganic speciation is provided in Figure 1. As indicated, three general approaches can be employed:

- Direct Analysis
- Dissolution followed by individual component determination
- Sequential extraction followed by elemental analysis of each fraction.

Vapor phase components are more readily speciated by virtue of their volatility as discussed later.

Direct analysis is conceptually a very attractive approach since there is very little likelihood for compound alterations during the analysis step. However, the techniques available for direct analysis suffer from a number of practical limitations in terms of sensitivity, specificity, and, in the case of X-ray diffraction, need for crystalline matrices. These limitations are often so severe that the technique is of no value for examining environmental samples. The features of these techniques are discussed more fully in a subsequent portion of this section.

The two alternative approaches to direct analysis, shown in Figure 1, involve dissolution of the atmospheric particulate sample into a liquid medium. Hence, both these approaches can lead to significant compound alteration due to oxidation, reduction or solvent complexation. In fact, one can seldom determine the original cation-anion pairs, i.e., specific inorganic compounds, from the data obtained. Nonetheless, these approaches are more generally useful than the direct analysis approaches since they can

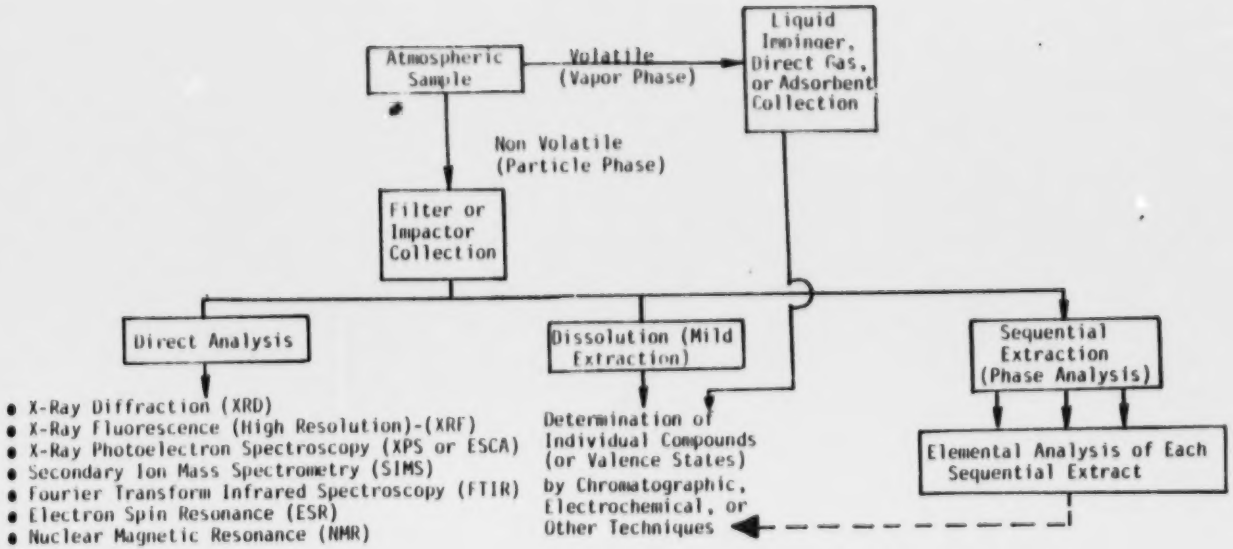
Atmospheric Sample
Volatile (Vapor Phase)
Liquid Impinger, Direct Gas, or Adsorbent Collection
Non Volatile (Particle Phase)
Filter or Impactor Collection
Direct Analysis
Dissolution (Mild Extraction)
Sequential Extraction (Phase Analysis)
• X-Ray Diffraction (XRD)
• X-Ray Fluorescence (High Resolution)-(XRF)
• X-Ray Photoelectron Spectroscopy (XPS or ESCA)
• Secondary Ion Mass Spectrometry (SIMS)
• Fourier Transform Infrared Spectroscopy (FTIR)
• Electron Spin Resonance (ESR)
• Nuclear Magnetic Resonance (NMR)
Determination of Individual Compounds (or Valence States) by Chromatographic, Electrochemical, or Other Techniques
Elemental Analysis of Each Sequential Extract

Figure 1. Diagram of potentially useful approaches to inorganic speciation.

utilize sensitive and relatively specific analytical techniques which require presentation of the sample in a dissolved state.

As shown in Figure 1, the first approach involves dissolving the sample in a mild extraction medium which tends to retain the original form (valence state, etc.) of the element of interest and analysis of the extract by such techniques as ion chromatography, gas chromatography (for a few selected volatile compounds), high performance liquid chromatography (HPLC), or electrochemistry (voltammetry). In this case the analytical techniques are chosen so as to provide qualitative (compound form, valence state) as well as quantitative information. Unfortunately, many of the inorganic species in particulate matter will not totally dissolve in mild extraction media, thus limiting the usefulness of this technique.

In the second case, sequential extraction, the sample is extracted with a series of liquid media of increasing aggressiveness in an attempt to separate the different chemical forms of the element. The extracts are then analyzed using common elemental analysis techniques such as atomic absorption spectroscopy (AAS) or inductively coupled argon plasma emission spectrometry (ICAP). Generally no attempt is made to identify the chemical form of the element in the sequential extracts, i.e., the extraction scheme serves as the separation/identification method Occasionally chromatographic or electrochemical approaches have been used in combination with selective extraction to yield more detailed speciation data. However, such schemes are relatively complex and still suffer from the potential alteration of compound states. The sequential extraction approach offers the potential for determining the crystalline phase distribution of a particular element. This feature can be important since the same inorganic compound can represent different health risks depending on the availability of the compound, i.e., the crystalline phase in which the compound is contained greatly affects the availability and, hence, the health risk associated with the compound

More detailed discussions of these three approaches are presented in the subsequent portions of this section.

DIRECT ANALYSIS

As indicated in Figure 1, direct analysis entails use of one or more instrumental techniques. A summary of the relevant characteristics of the potentially useful direct analysis techniques is provided in Table 1. As shown in this table all of the techniques have serious limitations which must be recognized when considering their use for solving a particular problem. Many of the techniques listed have been used only for a few selected elements or have not been applied to complex environmental samples and hence are unproven for most environmental applications.

X-ray diffraction (XRD) is capable of determining the concentration of crystalline materials, e.g., quartz, but is of only limited value in determining trace inorganic compounds of environmental interest since the concentration required for detection is relatively high. XRD has been employed for the determination of Pb compounds[4] as well as Zn and Cd

compounds[5] in atmospheric particulate samples and street dusts. However, in the latter study component concentrations were relatively high because the samples were collected near and/or within a smelting operation. XRD is of very limited utility in environmental analysis because of its inability to detect trace components and the requirement that analytes be present in a crystalline form.

X-ray fluorescence (XRF) is generally used for determination of the total concentration of an element. However, high resolution wavelength-dispersive instruments can distinguish valence states of certain elements. Sulfur speciation is the only reported example of environmental interest[6]. This particular application may be useful in an indirect sense to the speciation of As, Cr, Mn, or Ni since these elements can exist as sulfur compounds (sulfates or sulfides). XRF may be of only limited usefulness for direct speciation of these elements since chemical shifts in the fluorescence spectra, due to valence state, are probably not as large as for sulfur. However, further investigation of other elements is probably warranted to verify if such a limitation truly exists.

An advantage of both X-ray diffraction (XRD) and X-ray fluorescence (XRF) is that analytical data are obtained for the bulk sample. X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) and secondary ion mass spectroscopy (SIMS), on the other hand, examine only the surface layer (down to approximately 200 Å). While this feature may be attractive in certain studies, it is felt to be a severe limitation in most environmental applications since the bulk properties are of primary interest. XPS and SIMS can be used in combination with sputtering techniques to achieve greater depth profiles. In this approach the sample surface is eroded at a controlled rate using an argon ion beam while simultaneously collecting spectra, thereby mapping the composition as a function of depth. However, some evidence indicates that the sputtering technique alters the chemical form of many elements, thus making the speciation data suspect.

X-ray photoelectron spectroscopy (XPS) has been applied to environmental samples for a few elements (see Table 1). In one study[7] XPS was used to differentiate Cr(III) from Cr(VI) in sediments. XPS has been more widely used to differentiate between nitrogen and sulfur valence states[9]. While the differentiation of Cr valence states in solution is readily accomplished by wet chemical procedures, the XPS approach might be a useful confirmatory tool for such data since sample digestion is not required. However, the surface nature of the XPS data is certainly a limitation in this regard. The differentiation of nitrogen and sulfur chemical forms by XPS may be of indirect value in the current application since, as noted earlier, the four elements of interest (As, Cr, Mn, and Ni) can exist as nitrogen (nitrates) as well as sulfur (sulfates or sulfides) species.

Secondary ion mass spectroscopy (SIMS) is also a surface technique and hence of limited applicability. Classically SIMS (positive ion mode) has been used to determine the depth profile of a set of elements, without regard to chemical form. However, when the negative ion SIMS mode is employed, some information about the chemical form of the element can be gained. In one

TABLE 1. CHARACTERISTICS OF POTENTIALLY USEFUL TECHNIQUES FOR DIRECT ANALYSIS OF INORGANIC COMPOUNDS

Technique	Major Advantages	Major Limitations	References
X-ray Diffraction (XRD)	Yields compound specific data	Poor sensitivity. Requires crystalline material. Not apparently used for As, Cr, Mn, or Ni.	Pb(4) Pb, Zn, Cd(5)
X-ray Fluorescence (XRF) (high resolution)	Relatively straightforward to perform. Moderately sensitive.	Can provide speciation data only for a few elements, e.g., sulfur.	S(6)
X-ray Photoelectron Spectroscopy (XPS)	Can provide some information for noncrystalline materials	Not very sensitive. Primarily a surface technique; does not provide information on bulk composition.	Zn, Cr(7,) S, N, C(8) S, N(9)
Secondary Ion Mass Spectroscopy (SIMS)	Yields some information for noncrystalline materials. Good sensitivity.	Primarily a surface technique.	(10)
Fourier Transform Infrared Spectroscopy (FTIR)	Yields some information for noncrystalline materials	Some sample preparation required. Not highly specific or sensitive. Only useful for a few elements, e.g., S forms.	(11) (12)
Electron Spin Resonance (ESR)	Yields some information for noncrystalline materials	Not highly sensitive. Only useful for a few elements.	(13)
Nuclear Magnetic Resonance (NMR) (solids probe)	Yields some compound information for noncrystalline materials	Not highly sensitive. Only useful for a few elements.	(14)

study, furnace dust particles were examined by both negative and positive ion SIMS[10]. Some metal oxide clusters, e.g., MnO_4^-, were observed yielding a certain amount of chemical information.

The fact that SIMS is a mass specific technique makes assignment of chemical forms more direct than for other techniques such as X-ray photoelectron spectroscopy (XPS) where relatively small peak shifts are observed. However, the energetic nature of the SIMS process leads to a large amount of fragmentation thereby complicating the spectra and destroying some of the available speciation data. Consequently, while SIMS, especially in the negative ion mode, may be useful in some respects for the current application; it cannot be expected to yield unequivocal data and may be of no value for many complex samples.

Fourier transform infrared spectroscopy (FTIR) has been used to differentiate between inorganic compounds in coal and oil fly ash samples [11-12]. Although the approach can be applied directly to particle samples and yields surface composition data in this manner, the more common approach has been to separate water soluble from insoluble materials in order to simplify the matrix. Since the FTIR spectra are greatly affected by the hydration state of the compounds, careful, controlled pretreatment of the samples is required to yield a predictable hydration state.

The complexity of most environmental samples makes determination of trace components impossible using FTIR. Nonetheless, the technique may be of some value, especially when used in combination with data concerning elemental and anionic composition. The applicability of FTIR to the current problem (speciation of As, Cr, Mn, and Ni) is yet to be determined, although analysis of trace levels of these components in complex samples are probably not approachable by this technique.

Magnetic resonance techniques such as electron spin resonance (ESR) or nuclear spin resonance (NMR) have not been applied to environmental samples to any extent. ESR has been used to distinguish between Cr_2O_3 and CrO_2^- (both CrIII compounds) in simple mixtures[13]. The detection limit is reported to be ~2000 ppm for these compounds. Until recently NMR has been used exclusively for liquid samples. However, the introduction of the magic angle NMR technique has increased the research into solid materials. On the basis of relative sensitivity data, NMR might be useful for speciation of manganese and possibly arsenic but would be of virtually no value for chromium or nickel[14]. However, methods for introducing particulate samples into the NMR system have not been reported, i.e., the sample is normally distributed as a thin layer on a glass fiber filter.

While the magnetic resonance techniques have not been exploited for inorganic speciation in environmental samples, some potential exists. Considering the limited applicability of the available instrumental techniques, one should not completely disregard the development of magnetic resonance techniques for this application.

INORGANIC SPECIATION TECHNIQUES FOR DISSOLVED MATERIALS

This portion of the document describes the techniques available for conducting the "mild" extraction approach diagrammed in Figure 1. Because of the limited amount of information available on appropriate "mild" extraction procedures, this section primarily addresses the analysis steps. The subsequent portion of the section addresses sequential extraction approaches, and some of these approaches may be useful as preparation steps for the analytical methods described here.

In this approach the sample matrix is dissolved in such a manner as to retain the original form of the element of interest, to the extent possible; and subsequently the individual forms of the element(s) are determined by chromatographic, electrochemical, or other techniques. Obviously the dissolution process prevents direct determination of the inorganic compounds (cation/anion pairs) originally present in the sample. Determination of dissolved anion and cation concentrations separately by conventional techniques, e.g., ion chromatography and AAS, should generally be conducted as an indication of the original compound forms present.

While this approach is conceptually very useful, it too suffers from severe limitations, including the following:

(a) Nearly all forms of extraction have the potential of altering the valence state of the element of interest.

(b) Residual forms of the element will be left after extraction, except when very aggressive solvents are used. The residual material may represent either a different chemical form of the element or the desired form of the element retained within another phase of the sample matrix.

(c) To date this approach has been applied primarily to water samples, in which case the sample is already available in a dissolved form. Hence suitable extraction approaches have not been worked out for atmospheric samples except in a few selected cases.

The primary examples of this approach are in arsenic speciation wherein organoarsenates, arsenate, and arsenite are determined by various techniques including ion chromatography[15-16], ion-exchange or high performance liquid chromatography with elemental specific detection[17-19], gas chromatography [20], and selective hydride generation coupled to atomic absorption spectroscopy (AAS)[18]. A summary of available analytical techniques employed in this regard is contained in Table 2. Unfortunately nearly all of these studies deal exclusively with water matrices, and hence the problems associated with extraction from atmospheric particulate samples have not been addressed.

As shown in Table 2 most of the instrumental speciation techniques have been applied only to As species, with colorimetric analysis for Cr(VI) being the only major exception. The only methods shown in Table 2 which have been

TABLE 2. ANALYTICAL TECHNIQUES USED FOR INORGANIC SPECIATION IN SOLUTION

Technique	Matrix Studied	Species Determined	Extraction Procedure (for Solid Matrices)	References
Selective hydride generation; distillation; emission spectrometry	Various water types and atmospheric particle samples	As(III), As(V), methyl and dimethyl arsenic acid	--	(21, 22, 40)
Differential pulse polarography	Water	As(III), As(V)	--	(23) (18)
Ion chromatography	Water	AsO_4^{3-}	--	(16)
Ion chromatography coupled with hydride generation/AAS	Air particulate material	Methyl arsonic acid, dimethyl arsenic acid, and p-aminophenyl-arsonic acid; AsO_3^{3-}	Sonification in deionized water	(15)
HPLC with AAS detection	Water	AsO_3^{3-}, AsO_4^{3-}, methyl arsonic acid, dimethyl arsinic acid, arsenocholine and arsenobetasine	--	(18)
Ion exchange chromatography/AAS detection	Water	As(III), As(V), methylarsonic acid, dimethylarsenic acid	--	(19)
Adsorption on thiol cotton; selective hydride generation/ AAS detection	Water	As(III), As(V), Sb(III), Sb(V), Se(IV), Se(VI), TeIV, Te(VI)	--	(24)

TABLE 2. (Continued)

Technique	Matrix Studied	Species Determined	Extraction Procedure (for Solid Matrices)	References
HPLC/emission spectroscopy	Water	Diethyldithiocarbamates of Ni(II), Cu(II), and Co(III) compounds	--	(25)
Gas chromatography with flame photometric detection	Water	AsO_3^{3-}, AsO_4^{3-}, and methylarsonic acid as 2,3-Dimercaptopropanol derivatives	--	(20)
Colorimetric analysis as S-diphenylcarbazide complex	Atmospheric particulate material	Cr(VI) and total Cr; soluble versus insoluble total Cr	Extraction with base; conversion of one half of sample to Cr(VI) using permanganate for total Cr. Determination of Cr(VI) without permanganate oxidation.	ASTM Method D3586

applied to atmospheric particle samples are the work by Colovas, et al.[15] and Johnson and Braman[40], for organoarsenic compounds and the ASTM procedure for Cr(VI). Consequently, all the other methods listed require additional work to define a suitable sample preparation procedure.

Colovas[15] found organoarsenic compounds to be very unstable after extraction thus requiring analysis within 24 hours. Their study also indicated that the organoarsenic compounds of interest (see Table 2) existed exclusively in the particle phase and could be readily captured on Fluoropore® filters. Johnson and Braman[40] used glass fiber filters backed by silver coated glass beads to selectively capture volatile arsenic compounds.

The various instrumental speciation techniques presented in Table 2 are difficult to compare in a quantitative fashion. Each technique is unique and provides a different type of information. One would be well advised to use two or more techniques in parallel to gain more confidence in the data obtained. Electrochemical techniques are widely applicable but more subject to interference since they are not element-specific. Chromatographic techniques in conjunction with element specific detectors like those used in atomic absorption spectroscopy or inductively coupled argon plasma spectroscopy (AAS or ICAP) are much more specific but less generally applicable and more difficult to apply than electrochemical techniques. The selective hydride generation approach is convenient but is applicable only to As of the four elements of interest in this study.

A major concern in each of these techniques is the possibility of changes in valence state during the extensive sample pretreatment step. Although these approaches are more generally applicable than the direct instrumental techniques discussed in the previous section, they also suffer extreme limitations and require extensive development to become generally applicable to the current speciation problem.

SEQUENTIAL OR SELECTIVE EXTRACTION

As indicated in Figure 1 sequential extraction with media of increasing strength, followed by elemental analysis of each extract is another approach to inorganic speciation. Also covered in this section are selective, but non-sequential, extraction schemes which can be used in a similar manner. While this approach does not yield direct information as to the chemical form of the element, it does provide a convenient means of classifying inorganic materials in terms of their phase distribution and solvent reactivity. Such information can imply the presence of certain types of compounds but is subject to a high degree of uncertainty. This approach has been employed for solid samples by a number of workers[5, 26, 27]. Young[28] describes selective extraction approaches for numerous elements, including the four elements of interest in this study. However, these methods are intended for use in the analysis of ores where elemental concentrations are rather high.

A typical sequential extraction scheme[27] is shown in Figure 2. As indicated the fractions cannot be assigned to a particular compound or

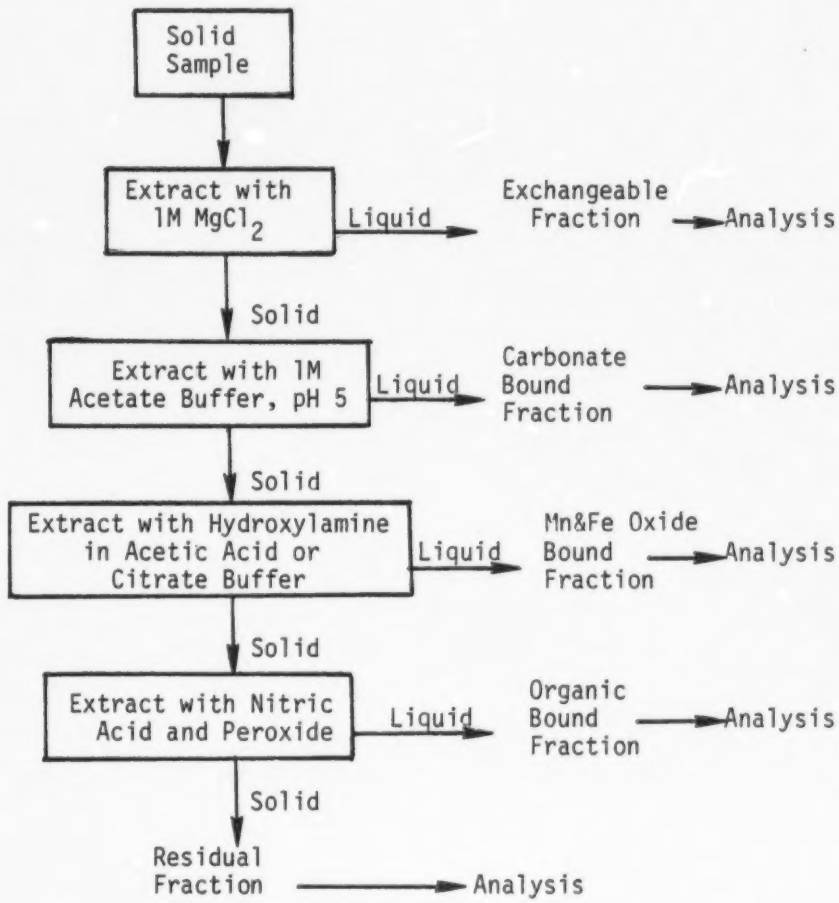

Figure 2. Typical sequential extraction scheme.(27)

element, although some compounds will tend to be present predominantly in a certain fraction. Nonetheless the procedure is useful as a general indication of the physical and chemical state of an element. The sequential or selective extraction approach can, of course, be used in combination with the more selective detection techniques discussed in the preceding section. However, the conditions employed in such extraction schemes may be harsh enough to alter the original form of the element, rendering the data from instrumental speciation techniques of little value.

Further discussion of particular sequential or selective extraction schemes is provided in Section 5 for the elements of interest. Based on our assessment of the literature;these approaches, while not providing direct chemical compound information, are potentially very useful as indicators of the physical and chemical form of each of the elements of interest. At a minimum these techniques can be useful when employed in conjunction with the direct analysis and/or analytical speciation techniques described earlier to provide confirmatory data.

SECTION 5

REVIEW OF CURRENT METHODOLOGY FOR SPECIATION OF METALS IN AMBIENT AIR

ARSENIC

Arsenic is classified chemically as a metalloid and belongs in Group VA of the periodic table. The principal oxidation states of arsenic in compounds are +3, +5, and -3. Simple ions of arsenic are not known. The major ore of arsenic is arsenical pyrite which makes up about 0.0005 percent of the earth's crust. It occurs commonly with nickel, copper, and tin and is recovered as the oxide As_2O_3 from flue dusts collected during pyrometallurgical extraction of these metals. The principal commercial form of arsenic is white arsenic, As_4O_6. Arsenic compounds are used mainly for their toxicity to living organisms.

Chemistry

Arsenic rarely occurs in the natural environment as the free element,but rather it is associated with sulfide ores in which it occurs as the metal arsenide. Arsenates, AsO_4^{-3}, of aluminum, boron, calcium, cobalt, copper, iron, lead, magnesium, manganese, uranium, and zinc occur naturally, probably as a result of weathering of the arsenide ores. Arsenic is found in rocks (igneous and sedimentary), in soils, in water and in living organisms.

Elemental arsenic can be obtained by the heating of the trioxide with carbon. The most stable form is called grey arsenic or the gamma allotrope. Other allotropic forms which are metastable have been described[29]. The element combines with many metals to form arsenides. It reacts with moist air at ambient temperatures to form a film containing the trioxide. It begins to oxidize in dry air at 200 C. Elemental arsenic reacts with the halogens to form the trihalides. With fluorine, the pentafluoride can also form. Arsenic reacts with sulfur to form As_2S_3, AsS, As_2S_5, and their mixtures. With sulfuric acid arsenic reacts to form the trioxide and SO_2. Hot dilute nitric acid slowly oxidizes arsenic to arsenious acid, H_3AsO_3. Concentrated nitric acid oxidizes it to arsenic acid, H_3AsO_4. No compounds in which arsenic has an apparent oxidation state of 0 are known.

As(-III)--Arsenides of metals are typical compounds in which the oxidation state is -3 and illustrate the element's nonmetallic characteristics. In compounds such as Na_3As, arsenic accepts electrons from true metals and achieves a formal charge of -3.

As(III)--The +3 oxidation state is the most stable and is characterized by the oxide, As_2O_3, the trichloride $AsCl_3$, the arsenite anion $(AsO_3)^{-3}$ and the sulfides. The vapor of the oxide exists as As_4O_6. The oxide is soluble in bases and acids (amphoteric) and exists as an amorphous glass or as the octahedral forms. As(III) is readily oxidized to As(V) by hot nitric acid, ozone, hydrogen peroxide, chlorine, bromine, iodine, and alkali hypochlorites. It can be reduced by Fehling's solution, stannous chloride and elemental copper in acid solution.

Arsenites in solution can reduce NO to N_2O. Arsenite salts can exist as orthoarsenites $(AsO_3)^{-3}$, pyroarsenites $(As_2O_5)^{-4}$, metaarsenites $(AsO_2)^-$ and the polyarsenites $(As_4O_7)^{-2}$, $(As_4O_9)^{-6}$, $(As_4O_{11})^{-10}$(30).

As(V)--As_2O_5 is a deliquescent white powder which dissolves slowly in water and decomposes at red heat to As_2O_3 and O_2. Arsenic acid, $H_3AsO_4 \cdot H_2O$, or acidic solutions of arsenate salts are oxidizing agents and liberate iodine from an iodide and chlorine from hot fuming hydrochloric acid. Salts exist as metaarsenates, $(AsO_3)^-$, orthoarsenates $(AsO_4)^{-3}$ and pyroarsenates $(As_2O_7)^{-4}$. The salts are isomorphous with phosphates.

Usage and Occurrence

Arsenic is 20th in abundance in the earth's crust and exists in minerals as the native element, arsenides, sulfides, sulfosalts, arsenites, arsenates, and silicates. Typical minerals:

realgar, As_2S_2
orpiment, As_2S_3
lollingite, $FeAs_2$
nickel glance, NiAsS
pharmacolite, $CaHAsO_4 \cdot 2H_2O$
mimetite, $3Pb_3(AsO_4)_2 \cdot PbCl_2$.

Arsenic, which is ubiquitous, enters the biosphere through industrial activity or through the use of arsenical products such as pesticides, medicines and feed additives. The three major sources of arsenic in air are smelting of metals from sulfidic ores, burning of coal, vegatation or agricultural wastes and the use of arsenical pesticides. The arsenic in air primarily exists as the oxide or one of the salts of the acids. However, it is removed from the air by settling or rainfall and therefore, atmospheric concentrations do not build up. Nonurban areas typically have maximal averages of 20 ng/m^3. However, in regions of high extractive metallurgical activity the concentration can reach 2.5 $\mu g/m^3$. Dusts and gases emitted from cotton gins can reach 100 $\mu g/m^3$. Burning of the cotton trash also discharges arsenic to the atmosphere(31).

Approximately 3 percent of the arsenic produced is used as metal in metallurgical alloys of lead and copper. The remaining 97 percent enters end-product manufacture in the form of As_2O_3. Manufacture of end-products for agricultural accounts for about 80 percent of the total consumption of arsenic. As_2O_3 is used to manufacture arsenical pesticides including the arsenate and arsenite salts of lead, calcium, and sodium and the organic

arsenicals. The compounds are used in insecticides, herbicides, fungicides, and as desiccants, algecides, sheepdips, wood preservatives, dyestuffs, and veterinary medications. High purity elemental arsenic and arsine (AsH_3) are used by the semiconductor and microelectronic industries[31].

Arsenic is present as a contaminant in by-product NaCl and Na_2SO_4 from the manufacture of cacodylic acid (dimethyl arsenic acid, $(CH_3)_2$ AsO(OH)) which is used in agriculture. The contaminated salts are recycled and reused or are disposed in a Class 1 landfill.

Arsenic cycling in the environment is constantly changing. It appears everywhere and is constantly being oxidized, reduced or otherwise metabolized. In the soils, insoluble or slightly soluble compounds of arsenic are being resolubilized. Man's activities have modified the arsenic cycle only by causing localized high concentrations.

Speciation Procedures

The arsenic compounds deemed to be of primary interest by the EPA Project Officer are listed in Table 3. Since most available techniques will not yield direct determinations for these compounds, the following discussion will indicate indirect approaches which can be useful in estimating concentrations for these compounds. The physical properties of the arsenic compounds listed in Table 3 are such that their presence in ambient air samples will be principally as particulate matter, with the possible exception of As_2O_3. Therefore, sampling of the air with the objective of differentiating between these arsenic species will involve particulate capture. Whether the removal of the particulate matter is done with a filter, impactor, or impinger should not have an influence on the distribution of the sample species present in air. Should any size partitioning occur during sampling, it is generally found that arsenic is more likely to be associated with the finer particles. If As_2O_3 is suspected to be present, care must be taken to minimize the amount volatilized during high volume sampling of ambient air. Impingers in series with the filter would capture any compound which is volatilized. Since dissolution of the arsenic compounds in acid or alkaline media appears to occur without reaction, i.e., change in oxidation state; speciation would still be possible.

None of the direct analysis methods discussed in Section 4 have apparently been used for arsenic speciation in environmental samples. Since arsenic generally is a trace component of particulate material, many of the direct analysis techniques do not have sufficiently good detection limits and/or selectivity for arsenic to be of any value. Secondary ion mass spectrometry (SIMS) has some potential for speciation of arsenic oxides but has not been evaluated for this application.

In view of the lack of suitable direct analysis methods, arsenic speciation methods must rely on the solution phase techniques described in Section 4. Since these techniques do not allow determination of cation/anion pairs originally present in the solid sample, one must rely on supportive data, e.g., ion chromatography, atomic absorption spectroscopy, to postulate

TABLE 3. CHEMICAL AND PHYSICAL PROPERTIES OF ARSENIC COMPOUNDS

Formula	Names (Mineral)	Color	Density g/cc	mp. C	bp. C	Solubility, 20 C g/100 ml H_2O
$NaAsO_2$	Sodium arsenite Sodium metaarsenite	Grey-white	1.87	-	-	Very soluble
$Pb_3(AsO_4)_2$	Lead orthoarsenate, also as di lead- and mono lead-orthoarsenate	White	7.30	1042(d)	-	Very slt. soluble Insoluble
$Pb(AsO_3)_2$	Lead metaarsenate	White	6.42(15C)	-	-	Decomposes
$Pb_2As_2O_7$	Lead pyroarsenate	White	6.85	802	-	Insoluble
$Na_3AsO_4 \cdot 12H_2O$	Sodium orthoarsenate mono- and dihydrogen	Colorless	1.88	120-130	180 ($-H_2O$)	35.09(34 C), 5.46 (0 C)
$NaAsO_3$	Sodium metaarsenate	Colorless	2.301	-	-	-
$Mg_3(AsO_4)_2$	Magnesium orthoarsenate (hoernesite: $8H_2O$) $22\ H_2O$ Monohydrogen: $7H_2O$ (roesslerite)	White White White	2.60-2.61	-	-	-
$Ca_3(AsO_4)_2$	Calcium orthoarsenate $3H_2O$	White White	- -	- -	- -	0.013
H_3AsO_4	Arsenic acid meta $HAsO_3$;ortho$\cdot 1/2H_2O$;pyro,$H_4As_2O_7$	White	2.0-2.5	35.5	160($-H_2O$)	16.7 others revert to orthoarsenic
As_2O_5	Arsenic pentoxide	White	4.086	315(d)	-	150(16 C)
AsO_3	Arsenic trioxide arsenolite, claudetite		3.865	315 sub 193	457.2	1.2(2 C) 2.04(25 C)

the original form of As in the sample. As shown in Table 2, a large number of solution phase speciation techniques exist for As. High performance liquid chromatography (HPLC) with atomic absorption spectroscopy (AAS) detection[18] and gas chromatography (GC) with flame photometric detection[20] have been used to differentiate between AsO_3^{3-} and AsO_4^{3-} in aqueous solution. In the latter technique the materials were reacted with 2,3-dimercaptopropanol to form volatile derivatives. These two approaches could be useful for distinguishing potassium arsenite, K_3AsO_3 from the various arsenates,e.g., sodium arsenate,of interest. However, the specific cation originally associated with the arsenate or arsenite anions can only be inferred from elemental analysis data.

Several methods listed in Table 2 are useful for distinguishing As(V), e.g., various arsenates, arsenic acid, arsenic pentoxide, from As(III) compounds, e.g., arsenic trioxide, various arsenites. These methods include selective hydride generation[22, 24], differential pulse polarography [18, 32], and ion-exchange chromatography with AAS detection[19].

While none of the arsenic compounds of special interest in this study are organoarsenates, speciation techniques for organoarsenates are of indirect interest as a means of determining the overall arsenic distribution. As shown in Table 2, such techniques include selective hydride generation/distillation[22, 40], ion-chromatography coupled with hydride generation/AAS[15], HPLC with AAS detection[16], and GC with flame photometric detection[20]. The work of Colovas, et al.[15] is particularly interesting since it addresses the analysis of several organoarsenic compounds in the atmosphere. These workers found all of the arsenic to be captured as particulate on filters with no indication of volatilization. Stability of the organoarsenates in the aqueous extract was found to be a significant problem.

Johnson and Braman[40], using a two-stage collector to distinguish volatile and nonvolatile forms of arsenic, reported that approximately 20 percent of the atmospheric arsenic was in an alkyl form (primarily dimethyl- and trimethyl-arsine).

Perhaps the most comprehensive arsenic speciation effort is that of Irgolic[18], who has developed and evaluated methods that allow determination of the valence states and compounds of arsenic in drinking water. Arsenate was determined by differential pulse polarography; organic and inorganic by high pressure liquid chromatography in conjunction with graphite furnace atomic absorption spectrometry. Arsenocholines, arsenobetaine, and iodoarsines were determined by mass spectrometry. The following methods were available at the time Irgolic's study was initiated for determining individual arsenic species compounds in water.[18]

(a) Use of silver diethyl-dithiocarbamate/colorimetry

(b) Use of ammonium molybdate to react with arsenate to form blue arsenomolybdate and determination colorimetrically. Arsenite is not affected.

(c) Polarography in acidic aqueous media; use of single sweep or a differential pulse polarography to determine arsenite. Arsenate is inactive. Aliphatic and aromatic arsenic and arsonic acids are reducible polographically. No report of differentiation of inorganic and organic species simultaneously had been reported.

(d) Hydride generation for arsenites, arsenates; alkyl and aryl arsenic acids, dimethyl arsenic acid; and trimethylarsine oxide. Speciation is done by pH selective reduction to arsines with atomic absorption spectroscopy (AAS) detection.

(e) Derivatization/gas chromatography for separation of methylarsenic acid and dimethyl arsenic acid using AAS detection.

(f) Gas chromatography/atomic absorption spectrometry for arsenite, arsenate, methylarsonic acid, dimethylarsinic acid, trimethylarsine oxide and methyl arsines.

(g) Gas chromatography/mass spectrometry for methyl arsines and ethyl, propyl, and butyl arsine.

The limitations of these seven speciation methods for arsenic compounds were the following:

- Methods were applicable only to the determination of a few arsenic compounds
- They required conversion to volatile derivatives
- Non-volatile arsenic compounds and arsenic compounds not reducible to volatile arsines can not be analyzed
- Solid phase compounds are not identifiable.

Unfortunately the application of the numerous arsenic speciation techniques to atmospheric samples requires a suitable extraction scheme which does not alter the form of the compound. Very little work has been conducted in this area to date. More research needs to be conducted to insure that extraction schemes capable of quantitatively dissolving the compound of interest without changing its valence state are available.

Several approaches to selective extraction (phase analysis) of As forms have been reported. Young[28] cited four methods of phase analysis of arsenic compounds in ores, flue dusts and reagents. (a) Arsenic pentoxide in arsenic trioxide was determined first by removing As_2O_5 with water in which it is more soluble then is the trioxide and using iodimetry, i.e., release of iodine from KI and titration with sodium thiosulfate. (b) Free arsenic trioxide in calcium arsenite can be determined by volatilizing As_2O_3 at 200-250 C. Calcium arsenite is stable up to 300 C. (c) Upon heating a mixture such as an arsenic ore with Al_2O_3 in a water vapor-CO_2-HCl atmosphere at 500-550 C, arsenido-sulfides decompose to yield H_2S and $AsCl_3$, while arsenites are volatilized as $AsCl_3$. Sulfoarsenates give H_2S and As_2O_5, and arsenates

give As_2O_5. Because of the solubility of As_2O_5 in hydrochloric acid, it can be separated from arsenides.

A scheme for the phase analysis of arsenic compounds in flue dusts was also cited and includes identification of the oxides, arsenates of lead and zinc, sulfides and metallic arsenic. Unfortunately the particulars were not given by Young[28].

Equally unfortunate is the fact that the distribution of specific arsenic compounds using various sequential extraction schemes, e.g., Figure 2, has not been evaluated. This could prove to be a useful objective for further research in this area.

Summary

Methods for arsenic speciation in water are prevalent in the literature. However, extraction schemes for either selective extraction of specific arsenic forms or extraction schemes for removing arsenic compounds without altering their oxidation state have not been widely reported or validated.

In view of the fact that direct analysis (without extraction) methods are not promising for arsenic speciation, the most useful approach to the problem is laboratory validation of extraction schemes for the arsenic compounds of interest. If such schemes can be validated to show that the form of the As is not altered, then the numerous speciation approaches available can be successfully applied.

CHROMIUM

Chromium,which is the first of three elements making up the periodic group VIB, makes up about 0.02 percent of the igneous rocks and ranks seventeenth in abundance among the nongaseous elements. The metal has widespread use as a decorative and protective metal, in corrosion resistant alloys and in compounds important to commerce such as the chromates. Chromates have been manufactured since the early 1800's by roasting chromite ores. Chromium is found in air, soil, water, and almost all living organisms.

Chemistry

Chromium is more abundant than nickel, zinc, and copper and ranks as the 21st element in the earth's crust in relative abundance. The principle ore is chromite which has the ideal composition of $FeO \cdot Cr_2O_3$. The ores are better represented as $(FeMg)O \cdot (Cr,Fe,Al)_2O_3$ in which the Cr/Fe ratio varies considerably. Metallurgical grade ore contains about 46 percent Cr_2O_3, i.e., Cr(III), chemical grade 40 to 46 percent Cr_2O_3, and refractory grade >20 percent Al_2O_3 or a combined Al_2O_3 and Cr_2O_3 equal to greater than 60 percent.

Chromium ion has oxidation states in compounds ranging from -2 to +6,but it most commonly occurs as 0, +2, +3, and +6. In nature however, only the trivalent and hexavalent forms are found. Since the trivalent oxidation state is most stable and hexavalent chromium is readily reduced to the

trivalent form by organic matter the trivalent form should prevail. However, hexavalent chromium exists in ores like crocoite, $PbCrO_4$[29, 30].

Chromium forms the following well-known series of compounds.

- Chromous compounds, CrX_2, contain divalent chromium; their chemistry resembles manganous and ferrous salts. The oxide, CrO, is strongly basic.

- Chromic compounds, CrX_3, contain trivalent chromium; their chemistry resembles ferric salts. The oxide, Cr_2O_3, is weakly basic and amphoteric.

- Chromium VI compounds which contain hexavalent chromium are analogous to sulfur trioxide. CrO_3 is strongly acidic, forming dichromate and chromate salts.

Metallic chromium is stable in air at ordinary temperatures but reacts with oxygen at elevated temperatures. Reactions with the halogens, carbon, sulfur, etc., take place at elevated temperatures. Chromium is oxidized by hydronium ion releasing hydrogen. Nitric acid dissolves chromium, but the chromium surface becomes passive in contact with concentrated nitric acid.

Cr(0)--

Chromium forms compounds in which the apparent oxidation state is zero. $Cr(CO)_6$ and $Cr(C_6H_6)_2$ are typical of those pi-bonded complex compounds. Their thermal decomposition leads to carbide containing metals. The carbonyl cannot be formed by direct reaction between CO and the metal. $Cr(CO)_6$ is a colorless, crystalline solid and is much more stable than $Fe(CO)_5$ or $Ni(CO)_4$. It is not oxidized in air and may be sublimed with decomposition. Perceptible decomposition occurs only above 140 C. It is stable toward chemical attack except by strong oxidizers such as Cl_2 or NO_3^-.

Cr(II)--

Chromous compounds behave similar to iron (II) compounds but are more strongly reducing. They will liberate hydrogen from aqueous acid solutions and are oxidized to Cr(III) by atmospheric oxygen. Chromium (II) acetate is water insoluble. Anhydrous and hydrated halides exist. CrS and CrO also exist as solids. Moist air will usually oxidize Cr(II) to Cr(III).

Cr(III)--

Chromic compounds resemble those of iron (III) but are more readily oxidized. They have the most stable oxidation state in aqueous solution. The ion is readily complexed to form octahedral, six-coordinate ions. Aquo-complexes exhibit amphoteric character. Chromium(III) can form chromites or hydrated oxides as well as the anhydrous oxide, Cr_2O_3. Insoluble anhydrous chlorides and bromides of Cr(III) exist.

Cr(VI)--

The chemistry of the +6 oxidation state of chromium especially CrO_4^{-2} is very much like that of SO_4^{-2}. It forms the trioxide, CrO_3, or chromic anhydride which is deliquescent and soluble in water. However, free chromic

acid does not exist. In acid solutions, the dichromate ion ($Cr_2O_7^{-2}$) is favored and is a powerful oxidizing agent. The hexavalent form of chromium, however, is relatively stable in water providing the concentration of organics or other reducing material is low. The reduced chromium is usually associated with the organics. Hexavalent oxygenated compounds can be adsorbed by clay particles.

Usage and Occurrence

Minerals containing chromium are primarily the oxides and are closely associated with the olivine and pyroxene type minerals. The most common ore is chromite which is a spinel containing Cr(III). Rarer minerals are chrome ochre, Cr_2O_3, and chromitite, $Fe_2O_3 \cdot 2Cr_2O_3$, and crocoisite. Major sources of chromite ore are found in Rhodesia, Philippines, Russia, etc., and ore is imported. Chromium occurs in minor amounts in many minerals in which Cr^{+3} replaces Fe^{+3} or Al^{+3} in the lattice forming chromium tourmalines, chromium garnets, chromium micas, and chromium chlorites. Elemental chromium is not found in nature. Chromium is found in soils, water, animals, plants, and in air. Emissions to the air originate in urban areas from coal-fired power plants (fly ash) and from wood burning as well as manufacturing operations. Trivalent and elemental chromium in air should not undergo any reaction. Hexavalent chromium in air could eventually be reduced with dust particles and other pollutants to form trivalent chromium. However, the forms and reactions of chromium in air have not been extensively studied[33].

Since there has not been any mining of chromite ore in the United States since 1961, the source of chromium and its compounds in air pollution comes primarily from industrial processes and the use of products from these processes.

Chromite ore with the higher Cr_2O_3 content is used to prepare ferrochrome used in stainless steel and other steel alloy production. If the ores contain chromium at the 30 percent level, it is used to make refractories for melting furnace linings (mp 2040 C). Ores with about 45 percent chromium are used for the preparation of chromium-VI based chemicals. Chromate and dichromate salts are used as tanning agents, pigments, catalysts, electroplating, and wood preservatives.

$Cr(CO)_6$ is prepared through specialized reactions involving Grignard reagents and cannot be synthesized directly from elemental chromium and CO.

Speciation Procedures

The particular Cr compounds deemed to be of primary interest are listed in Table 4. The properties of these chromium compounds suggest that their presence in ambient air samples will be primarily as particulate materials, except for chromium carbonyl. Therefore, sampling the air for such chromium species will require the capture of particulates. Dusts and fumes of chromium compounds may be collected by any method suitable for collection of other dusts and fumes, i.e., filters, electrostatic precipitators, and impactors. Chromic acid (CrO_3), which is very hygroscopic,could exist as mist and would require capture by impinger. In addition, in the presence of moisture any soluble Cr(VI) compound is amenable to reduction by dust

TABLE 4. CHEMICAL AND PHYSICAL PROPERTIES OF CHROMIUM COMPOUNDS

Formula	Name (Mineral)	Color	Density g/cc	mp. C	bp. C	Solubility 20 C g/100 ml H_2O
$Cr(C_2H_3O_2)_3 \cdot H_2O$	Chromic (III) acetate	Grey-green	-	-	-	Soluble
$Cr(C_2H_3O_2)_2$	Chromous (II) acetate	Red	1.79	-	-	Slt. soluble
$Cr(CO)_6$	Chromium (0) carbonyl	Colorless	1.77(18)	subl. 20 C	151 (d)	Insoluble
Cr_2O_3	Chromium sesquieoxide	Green	5.21	2435	ca 3000	Insoluble
$(Cr_2O_3 \cdot XH_2O)$	Chromic (III) oxide	Gray-green	-	-	-	Insoluble
CrO_3	Chromium (VI) oxide Chromium trioxide Chromic anhydride	Red	2.70	196	(d)	166(15 C)
$CaCrO_4 \cdot 2H_2O$ $CaCrO_4$	Calcium chromate (VI) sintered	Yellow	-	200 ($-2H_2O$)	-	16.3; 22.4(0 C)
$PbCrO_4$	Lead chromate (VI) (crocoite) Chrome yellow	Yellow	6.3	844	0	5.8×10^{-6} (25 C)
$Pb_2(OH)_2CrO_4$	Basic lead chromate (VI)	Red	-	920	-	Insoluble
$PbCrO_4 \cdot PbO$	Basic lead chromate (VI) Chrome red Lead chromate (VI) oxide	Red	-	-	-	
$SrCrO_4$	Strontium chromate (VI)	Yellow	3.895 (15 C)	-	-	0.12 (15 C)

TABLE 4. (Continued)

Formula	Name (Mineral)	Color	Density g/cc	mp. C	bp. C	Solubility 20 C g/100 ml H_2O
K_2CrO_4· $ZnCrO_4$	Potassium zinc chromate VI	Yellow	-	-	-	-
(FeMg)O· $(CrFeAl)_2O_3$	Unroasted chromite (III) ore	Black	4.32-4.57			
Na_2CrO_4, Na_3AlO_2, Na_2SiO_3 $CaSiO_3$, Ca_3AlO, $CaCrO_4$ $MgSiO_3$, Mg_3AlO_3, $MgCrO_4$ Fe_2O_3 + Residues	Roasted Chromite Ore*					Na_2CrO_4 soluble

* A typical mixture and conditions are: Ore 24 parts; soda ash 15 parts; lime 12 parts; residue 49 parts (recycle) roasting temperature 1100-1150 C for four hours. Lime added to increase roasting rate and render alumina + silica values insoluble.

particles containing organic residues. $Cr(CO)_6$ sublimes at ambient temperatures; and if isolated as a solid from the atmosphere, it would be lost through the filter[34].

In general, speciation of chromium deals with the differentiation between the chromium present in samples as Cr(III) or Cr(VI). Since Cr(VI) has been associated with health hazards, its determination in the sample is particularly important. Cr(III) is considered to be of less concern and is an essential trace element form in human biological function. This differentiation is especially important in ambient air samples and of course water samples where the likelihood of both forms existing is greater than in biological specimens, food, and soils. In air samples, Cr(VI) may be present as both water soluble and water insoluble forms. This partitioning has been addressed in the characterization of occupational air samples.

Some direct instrumental analysis of chromium on solid materials has been conducted. These techniques include X-ray photoelectron spectroscopy (XPS)[7] and electron spin resonance (ESR)[13]. Although XPS appears to be capable of distinguishing Cr(III) from Cr(VI), it probably does not have sufficient resolution to distinguish between compounds with the same chromium valence states. The ESR technique is capable of distinguishing Cr_2O_3 from $NaCrO_2$, both Cr(III) compounds, but its sensitivity is probably not adequate for most environmental applications. Because of these limitations, solution phase methods for speciating Cr appear to be more useful than the direct analysis approaches.

The most commonly used approaches for Cr speciation are methods similar to ASTM D3586. In this method the atmospheric particle sample is extracted with base. One half of the sample is oxidized with permanganate to convert all chromium forms to Cr(VI). The oxidized and untreated portions of the sample are then analyzed for Cr(VI) using a colorimetric technique to yield values for total soluble Cr and Cr(VI), respectively. The difference between total soluble Cr and Cr(VI) is assumed to be Cr(III) since the other possible valence states are not commonly present in the atmosphere. However, there does not appear to have been a rigorous evaluation of this method for samples containing known levels of the compounds of interest. This avenue probably could be a useful area for further research.

Both gas chromatography (GC)[35] and differential pulse polarography[36] have been used to speciate dissolved chromium. The GC technique involves forming the trifluoroacetylacetonate of Cr(III) at 170 C and determining this derivative by GC with electron capture detection. Since most other metals form acetylacetonates at room temperature, they can be removed prior to formation of the Cr(III) acetylacetonate[37]. Neither of these reports describe the behavior of Cr(VI) towards the derivatizing reagent. This aspect of the methods deserves further attention.

The polarographic approach referenced above detects Cr(VI) and appears to be free of other common metal interferences when applied to natural water samples. However, the selectivity of the method for complex atmospheric particulate samples needs careful evaluation before the approach can be considered viable. Cr(III) is not detected by the method.

Selective or sequential extraction schemes for chromium have not been widely reported. Young[28] could find only two literature citations on the selective or extraction phase analysis of chromium. Neither of these citations were relevant to determining Cr(VI) in particulates. The methods cited were used for differentiation between $CrCl_3$(III) and $CrCl_2$(II) and Cr_2N and CrN.

With regard to the compounds listed in Table 4, none of the existing methods are capable of unambiguously determining their concentration. Use of the Cr(III) and Cr(VI) speciation methods in conjunction with elemental analysis (e.g., AA) of other metals (Ca, Pb, Sr, etc.) and anion analysis (e.g., ion chromatography) will provide some indirect information. Capture and analysis of volatile $Cr(CO)_6$ will require use of impingers containing organic solvents. Although instrumental methods for $Cr(CO)_6$ have not been reported, some of the methods described for $Ni(CO)_4$ may be useful.

Summary

The available direct analysis techniques for Cr do not appear very promising because of sensitivity and resolution limitations. XPS (ESCA) can provide a limited amount of information concerning valence states but is limited to surface analysis.

Speciation methods for dissolved chromium are capable of distinguishing Cr(III) and Cr(VI). More detailed speciation approaches have not been reported. Selective or sequential extraction of chromium from relevant solid materials have not been reported.

In view of these findings, the most productive approach to the development of chromium speciation methods would be to evaluate the validity of the existing Cr(III) and Cr(VI) speciation procedures by introducing known levels of compounds onto particulate matter and processing this material through the procedure. Some additional work on X-ray photoelectron spectroscopy (XPS) analysis may also be warranted as a means of supporting the wet chemical data.

MANGANESE

In past studies[38], it has been difficult to differentiate between natural sources of manganese and those originating from anthropogenic activities. Emissions from man's activities include beneficiation by crushing, heavy media separation, jig table flotation, and magnetic separation. Large quantities of manganese are also used in the production of steel and other alloys and in the manufacture of dry cell batteries.

Chemistry

Manganese is one of the more abundant elements in the earth's crust, is widely distributed in the terrain,and it is present in nearly all organisms. It is closely associated with iron and similar in its chemical behavior. In its compounds, manganese can have oxidation states of +1, +2, +3, +4, +6, and

+7. Compounds are also known in which manganese has oxidation states of -3, -1, 0, +5. The most stable salts (compounds) contain the divalent oxidation state of manganese while tetravalent manganese forms the most stable oxide, i.e., MnO_2 [29, 30].

Elemental manganese is a rather powerful reducing agent. It can be oxidized by hydrogen ion, H_2O, the halogens, and sulfur to the dipositive state. Oxygen reacts with elemental manganese to form the oxide, Mn_3O_4; carbon reacts to form the carbide, Mn_3C; and nitrogen can react to form the nitride, Mn_5N_3. Chemical characteristics of the other oxidation states are given below.

Mn(II)--
Manganous (II) compounds are strongly basic and resemble chromium (II) and iron (II) compounds in solubility and crystal structure.

Mn(III)--
In alkaline medium tripositive manganese (manganic compounds) is obtained even by atmospheric oxidation, e.g. $MnO(OH)$ formed from $Mn(OH)_2$ precipitates. However, Mn(III) is unstable in aqueous solution and disproportionates to Mn(IV) and Mn(II). Mn(III) is stabilized as insoluble salts such as the orthophosphate or as a complexed ion such as $(Mn(CN)_6)^{-3}$.

Mn(IV)--
The most common compound is the dioxide. It is a powerful oxidant and is readily reduced to Mn(II). Mn(IV) salts are rare, but they do form manganites ($CaMnO_3$).

Mn(VI)--
Hexapositive manganese is known in the form of the manganate ion, MnO_4^{-2}, and is similar to CrO_4^{-2} and FeO_4^{-2} ions in the solubilities of its compounds. Mn(VI) will disproportionate in acidic solutions, even in carbonic acid, to form Mn(VII) and Mn(IV) but is stable in alkaline solutions.

Mn(VII)--
The permanganate ion, MnO_4^-, is the best known form of this oxidation state. In solubilities and crystal structures permanganate compounds are comparable to perchlorate compounds (ClO_4^-). Most reductants convert Mn(VII) to Mn(II) in acid solution.

Mn(0)--
The manganese carbonyls and the organocarbonyls, e.g., cyclopentadienyl manganese tricarbonyl, are examples of volatile manganese compounds synthesized by man and used in commerce.

Some chemical and physical properties of chemical compounds of interest to ambient air sampling are given in Table 5. Another aspect of the chemistry of manganese that may have an effect on the form of manganese in the atmosphere is the colloidal properties of hydrous manganese dioxide. The surfacial effects are created by the OH groups exposed at the surface which are capable of adsorbing charged species such as other metal ions. The

surface charge is pH dependent, and the MnO_2 isoelectric point occurs at pH 2[39].

Mn in the form of an oxide is known to catalyze the oxidation of SO_2 to SO_3 (or sulfuric acid) absorbed on its surface. $MnSO_4$ and MnS_2O_6 (dithionate) are formed. This reaction is utilized in flue gas desulfurization. In addition, the oxide will react with any NO_2 in the atmosphere to form $Mn(NO_3)_2$ at the surface. The nitrate is unstable on heating to ~150C and is decomposed back to the oxide and NO_x.

Usage and Occurrence

Minerals containing manganese include sulfides, anhydrous and hydrous oxides, carbonates, anhydrous and hydrous silicates, anhydrous and hydrous phosphates, arsenates, tungstates and borates. Manganese is a trace constituent in many more minerals. The minerals are widely distributed in the earth's crust (~0.1 percent of crust). It is the twelfth most abundant element on earth. Principal minerals are

pyrolusite, MnO_2
psilomelane, $BaMnMn_8O_{16}(OH)_{14}$
manganite, $Mn_2O_3\ H_2O$
hausmannite, Mn_3O_4.

Other minerals are listed in Table 5 under their chemical names.

The National Research Council (NRC)[38] study suggested that manganese occurs in nature in constantly changing complex relations involving physical, chemical, and biological activity with the oxide being the dominating species. The NRC Report concluded that any study of past data on manganese in ambient air, "must cope with variations resulting from different methods of sampling and analysis which are of uncertain reliability and interpretation". It was also concluded that manganese in the atmospheric precipitation was primarily the result of man's activities.

Besides being used in the manufacture of steel and other metal alloys, manganese is used in fertilizers, feed additives, ferrites, ceramic and glass colorants, hydrometallurgy of uranium and zinc, welding rods, fluxes as well as for dry cell battery manufacture.

Speciation Procedures

Very little work has been conducted in the area of Mn speciation. Negative ion selective ion mass spectrometry (SIMS) was used to indicate certain manganese oxide fragments but was not evaluated in detail for this purpose[10]. Electron spin resonance (ESR)[13] and nuclear magnetic resonance (NMR)[14] techniques have not been extensively evaluated but may be of some value as direct analysis methods in the future.

Neither chromatographic nor electrochemical speciation methods for Mn were found in the literature. The only speciation approaches for Mn which have been evaluated are sequential extraction schemes. Tessier[27], using

TABLE 5. CHEMICAL AND PHYSICAL PROPERTIES OF MANGANESE COMPOUNDS

Formula	Name(s) (Mineral)	Color	Density g/cc	mp. C	bp. C	Solubility 20 C g/100 ml H_2O
MnO	Manganese monoxide Manganese (II) oxide (manganosite)	Green	5.45	1650	-	Insoluble
MnO_2	Manganese dioxide Manganese (IV) oxide (pyroluskite)	Black	5.026	535(-O_2)	-	Insoluble
Mn_2O_3	Manganese sesquioxide Manganese (III) oxide (manganite)	Black	4.50	1080(-O_2)	-	Insoluble
Mn_3O_4	Trimanganese tetroxide Manganese (II,III) oxide (hausmannite)	Black	4.586	1705	-	Insoluble
$MnSiO_3$	Manganous meta silicate Manganese (II) silicate (rhodonite)	Red	3.72	1323	-	Insoluble
Mn_2SiO_4	Manganous orthosilicate (tephraite)	Red	4.043	1300	-	-
$MnCO_3$	Manganous carbonate Manganese (II) carbonate (rhodocrosite)	Pink to Brown	3.125	(d)	-	0.0065 (25 C)
$MnSO_4$	Manganous sulfate Manganese (II) sulfate (0, 1, 4 and 5 hydrated salts)	Reddish	3.25	700	850(d)	52 (5 C)

TABLE 5. (Continued)

Formula	Name(s) (Mineral)	Color	Density g/cc	mp. C	bp. C	Solubility 20 C g/100 ml H_2O
$Mn(NO_3)_2 \cdot 6H_2O$	Manganous nitrate Manganese (II) nitrate	Rose	1.82	25.8	1294 (d)	426 (0 C)
MnS_2O_6	Manganous dithionate Manganese (II) dithionate	-	1.757	-	-	Soluble
$Mn_2(CO)_{10}$	Dimanganese pentacarbonyl	Yellow	1.75	154-155	-	Insoluble

the extraction scheme shown in Figure 2, found Mn in river sediment to be present primarily in the "residual" fractions, with a smaller amount present in the "exchangeable", "Fe/Mn oxide-bound", and "carbonate" fractions. Unfortunately, no work was conducted with authentic compounds to examine their partitioning behavior in the extraction scheme. Selective or sequential extraction (phase analysis) schemes for manganese have been reported but were used only in ores and compounds. Very little has been done with the determination of trace amounts in ambient air samples. Young[28] reported chemical dissolution and filtration approaches to separating Mn(II), Mn(III), and Mn(IV) using ammonium hydroxide and ammonium chloride to dissolve Mn(II) and 2N sulfuric and hydrofluoric acids to dissolve Mn(III). The residue was analyzed for Mn(IV). Procedures for the separation of elemental Mn from MnO are also mentioned. No mention was made of the utility of these techniques for speciation of manganese compounds present in trace amounts. This area would appear to be the most useful area for further research into manganese speciation.

Organic manganese carbonyl complexes can be determined by gas chromatography with element specific detection although such techniques have not been applied to $Mn_2(CO)_{10}$ itself.

Summary

Manganese speciation efforts have been extremely limited, and no proven methods are available. Although no highly promising techniques are available for air sample characterization, the areas of selective or sequential extraction and possibly direct analysis, e.g., selective ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and nuclear magnetic resonance (NMR) may warrant further study.

NICKEL

Nickel makes up about 0.01 percent of the earth's crust and is usually found as the sulfide mineral pentlandite. The metal is used in the production of corrosion resistant alloys of steel, chromium, and copper-zinc.

The metal is recovered from the beneficiated sulfide ore by roasting in the presence of silica which is used to capture iron in the form of a slag. The nickel oxide is reduced to the impure metal with water gas. Final purification is accomplished via the Mond process in which the impure metal is reacted with carbon monoxide at 60 C to form the volatile $Ni(CO)_4$. The nickel carbonyl is decomposed on a bed of nickel particles at about 200 C and the CO recycled. Other methods of purification of the impure nickel are based on pyrometallurgy and electrochemical processes[29, 30].

Chemistry

Nickel is a moderately strong reducing agent and is comparable to iron and cobalt, the other two elements making up the ferrous metal triad of the first transition metal series. Hydrogen ion will react with the metal to form divalent ions. Stronger oxidizing agents such as fluorine, chlorine,

bromine, oxygen, and nitric acid will react to form the divalent ion. Nickel (II) is the most important oxidation state, and other oxidation states observed are 0, +1, +3, and +4.

Ni(II)--

Compounds of the dipositive nickel resemble those of chromium (II) and manganese (II). The chemistry of cobalt (II) and nickel (II) are so similar that it is difficult to separate the two species. The dipositive ions form a variety of complexed species with a variety of donor molecules or ions especially those containing oxygen, nitrogen, or sulfur in the molecule or ion. Complexed nickel (II) species can exhibit the square planar, octahedral and tetrahedral geometric configurations.

Ni(I,III,IV)--

Both Ni(I) and Ni(III) compounds are rare. Ni(III) exists in the oxide, Ni_2O_3, but exist only as hydrates of this sesquioxide, e.g., as $NiO(OH)\cdot XH_2O$. The hydrated Ni(III) oxide is formed from the hydrated (+2) oxide by reacting nickelous salts with a strong oxidizing agent such as an alkali hypochlorite. The hydrate of nickel (IV) oxide, NiO_2, is a strong oxidizing agent and is the depolarizing agent in the Edison storage cell. No examples of simple +4 ions are known.

Ni(0)--

Nickel has an apparent oxidation state of zero in the tetracarbonyl, $Ni(CO)_4$. Thermal homogeneous gas phase decomposition leads to extremely fine Ni particulates;and if air is present, the vapors can explode yielding CO_2 and particulate elemental nickel.

Usage and Occurrence

Minerals containing nickel include sulfides and the hydrous and anhydrous silicates and oxides. The principal sulfide mineral is pentlandite, $(NiFe)_9S_{16}$, which is found associated with chalcopyrite, $CuFeS_2$. The main oxide minerals are the laterites which were formed by the weathering of nickel-bearing rocks in tropical (or once tropical) regions followed by secondary deposition of nickel oxides and silicates, e.g., nickeliferous iron laterite which is a hydrated iron oxide with nickel dispersed throughout. The hydrous silicate mineral garnierite contains nickel silicate in solid solution of hydrated magnesium and iron silicates, $(NiMg)SiO_3\cdot XH_2O$. Although laterite ores are the largest reserve of nickel, they are widely distributed in the earth's crust.

The sulfide ores yield nickel by a combination of pyrometallurgical processes followed by either electrolytic refining, refining via formation of the tetracarbonyl or by a hydrometallurgical process. Lateritic ores are processed primarily through pyrometallurgical processes.

Among the uses for nickel oxides are the charge alloying of steel and the manufacture of frits, ferrites, ceramic and glass colorants, and catalysts. Salts of nickel are used in metal finishing, electrorefining, electroless plating and the preparation of catalysts and other salts, impregnated carbon (for gas masks), pigments, and dye mordants. The oxide is

added to plastics as an ultraviolet light absorber and used in organic dyes and pigments, agricultural chemicals, fuel cells, specialty ceramics, and photography[41].

Nickel compounds important in commerce include sulfates, chlorides, carbonates, acetates, and sulfides. About 44 percent of the nickel consumed is used in stainless steel, 33 percent as nonferrous and high temperature alloys, 17 percent in electroplating and 6 percent in the production of catalysts, ceramics, magnets, and salts.

Nickel in atmospheric emissions occurs from natural and anthropogenic sources. Natural sources of nickel in the atmosphere, which make up about 35 percent of the total emission, originate from wind blown soil, volcanoes, vegetation, forest fires, sea salt, and meteoric dust. Anthropogenic sources of the emissions are from direct sources primarily from mining, smelting, and refining of nickel-bearing ores, secondary and co-product nickel recovery, alloy production, electroplating, and battery and nickel chemical manufacturing. Inadvertent sources,i.e., those that emit nickel or nickel compounds into the atmosphere unintentionally, are coal and oil combustion, coke production, municipal refuse incineration, petroleum processing, coal conversion processing, cement manufacturing, and asbestos mining. Of the inadvertent sources of nickel emissions to atmosphere, fuel combustion makes up 85 to 95 percent.

Speciation Procedures

It can be seen from the physical properties of the nickel compounds listed in Table 6 that their presence in ambient air samples will be principally as particulate matter. Even the gaseous compound, $Ni(CO)_4$, is so reactive with air that its combustion (oxidative decarbonylation) will produce particulate elemental nickel in ambient air in a relatively short time. Therefore, sampling the ambient air for nickel compounds will involve the capture of particulate material on filters and/or impactor surface if segregation by particle size is desired. As with other particulates captured during ambient air sampling, the presence of the filter imposes limitations on the direct determination of the forms of nickel isolated from the air sample.

When particulate emissions from coal and fuel oil fired plants are part of the captured material, smaller particles are usually richer in nickel. Therefore, sample collection methods with size segregation capability can provide some partitioning.

Only FTIR has been reported as a direct speciation method for Ni[11]. The specificity of this approach is not particularly good, and its applicability to trace nickel concentrations is somewhat in doubt. Although X-ray photoelectron spectroscopy (XPS) and selective ion mass spectroscopy (SIMS) may be useful speciation methods for nickel, they have not apparently been evaluated for this purpose.

Ni(II) has been determined in solution, as a diethyldithiocarbamate derivative, using HPLC with atomic emission detection[25]. The applicability

TABLE 6. CHEMICAL AND PHYSICAL PROPERTIES OF NICKEL COMPOUNDS

Formula	Name (Mineral)	Color	Density g/ml	mp. C	bp. C	Solubility 20 C g/100 ml H_2O
Ni	Nickel	Silver	8.90	1455	2900	Insoluble
NiO	Nickel monoxide (bunsenite)	Green-Black	7.45	2090	400 (to Ni_2O_3)	Insoluble
Ni_2O_3	Nickel sesquioxide	Gray-Black	4.83	600 ($-O_2$)	-	Insoluble
$Ni_2O_3 \cdot XH_2O$	Nickel hydroxide	Gray-Black				
NiS	Nickel monosulfide (millerite)	Black	5.3-5.65	797	-	0.00036(18 C)
Ni_3S_2	Nickel subsulfide (heazlewoodite)	Bronze	5.82	-	-	Insoluble
$NiSO_4$	Nickel sulfate	Yellow	3.68	840($-SO_3$)	-	29.3(0 C)
6 H_2O	Nickel sulfate	Blue	2.07	-	280($-6H_2O$)	62.5(0 C)
7 H_2O	(morenosite)	Green	1.948	31.5($-H_2O$)	103($-6H_2O$)	75.6(15.5 C)
$NiCO_3$	Nickel carbonate	Green	-	(d)	-	0.009 (25 C)
$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	Nickel basic carbonate (zaratite)	Green	2.6	-	-	Insoluble
$Ni(C_2H_3O_2)_2$	Nickel acetate	Green	1.798	(d)	-	16.6
	also as $\cdot 4H_2O$		1.744	(d)	-	Soluble
$NiCl_2$	Nickel chloride	Yellow	3.55	sublimes	973	64.2
	also as $\cdot 6H_2O$	Green				254
$Ni(CO)_4$	Nickel carbonyl	Colorless	1.32	-25	43	0.018(9.8 C)

of this and similar approaches for other nickel species has not apparently been investigated. This approach may be a useful area for further research.

Selective or sequential extraction methods for distinguishing between metallic nickel, oxide nickel, and sulfide nickel have been compiled from a wide range of literature by Young[28] under the category of phase analysis. Metallic and sulfide nickel have been differentiated from the oxide form by leaching with a chlorine (or bromine)/methanol solution. The oxide of nickel remains insoluble,while elemental nickel and sulfide nickel dissolve. The method is judged empirical and the results approximate. The procedure, developed for characterization of extractive metallurgical products, would have to be modified for particulates. Nickel metal can be separated from nickel oxide by the selective dissolution with a solution of mercuric chloride. The oxide remains in the residue,and the elemental nickel is in the filtrate. Both can be analyzed for nickel by a suitable method.

The amount of metallic nickel in a solid can also be determined by the hydrogen evolved during treatment with acid. The amount of elemental nickel on a substrate catalyst support, mixed with nickel oxide or nickel sulfide can be determined in this manner. Nickel sulfide can be selectively dissolved from nickel and nickel oxide by treating the mixture with a solution of ammonium nitrate and strong hydrogen peroxide. Methods for the separation of nickel oxide, sulfide, and silicate and the determination of metallic nickel in the presence of nickel oxide are also reported[28].

Tessier[27] evaluated the nickel distribution in river sediments using the sequential extraction scheme shown in Figure 2. Most of the nickel was found in the "residual" fraction, and a small amount (20 percent) was found in the "Fe/Mn oxide-bound" fraction. No specific nickel compounds were evaluated using the scheme.

Two methods have been reported for nickel carbonyl, $Ni(CO)_4$. Stedman, et al.[42] reported a chemiluminescence technique based on reaction with O_3 and CO. Improvements were made on the technique by Houpt, et al.[43]. A mass spectrometric method was used to determine $Ni(CO)_4$ in automobile exhaust[44]. These two techniques are direct methods not requiring isolation of a discrete sample, an advantage for such an unstable compound.

Summary

While several direct analysis approaches and instrument "solution phase" speciation approaches may be useful, none have been evaluated in detail. Consequently, a fruitful area for further research could be the evaluation of a few of these methods, e.g., XPS, SIMS, chromatographic methods.

A number of selective and sequential extraction procedures have been used for nickel speciation. However, none of these have been evaluated using authentic components in a relevant matrix. Such an evaluation would probably be a most useful area for further research into nickel speciation.

The volatile $Ni(CO)_4$ compound, while highly unstable in air,can be determined using mass spectrometry and chemiluminescence techniques. Such

direct techniques are required for $Ni(CO)_4$ determination because of its instability.

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